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## Review

Radu Malureanu\* and Andrei Lavrinenko

# Ultra-thin films for plasmonics: a technology overview

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**Abstract:** Ultra-thin films with low surface roughness that support surface plasmon-polaritons in the infra-red and visible ranges are needed in order to improve the performance of devices based on the manipulation of plasmon propagation. Increasing amount of efforts is made in order not only to improve the quality of the deposited layers but also to diminish their thickness and to find new materials that could be used in this field. In this review, we consider various thin films used in the field of plasmonics and metamaterials in the visible and IR range. We focus our presentation on technological issues of their deposition and reported characterization of film plasmonic performance.

**Keywords:** plasmonics; ultra-thin films; VIS/IR range.

## 1 Introduction

Plasmonics currently lives through the revival period after its first successful appearance in the 1980s with findings summarized in Raether's monograph [1]. In his broad overview of perspective developments in paradigm of CMOS compatible silicon photonics, Richard Soref mentions plasmon optics or plasmonics as one of the photonics key instrument to reach extreme light localization, deep subwavelength resolution and enhanced light emission [2]. Such properties stem from light-free electron coupling occurring at metal-dielectric interfaces. The carriers of such interaction are surface plasmons, which occur in two basic configurations: localized surface plasmons with

deep analogy in mechanical oscillations and surface plasmon-polaritons (SPPs) or propagating surface plasmons analogous to mechanical waves [3]. In this review, we will focus on fabrication issues mostly related to SPPs propagation. By coupling to the ensemble of free electrons, light can be effectively confined and, as a result, guided. For such alliance of characteristic temporal parameters in correspondence with optical frequencies and spatial parameters of electronic footprints, plasmonics has been intensively praised for bridging photonics and electronics. A special direction of plasmonic circuitry has been successfully propelled for a while, see, for example [4].

However, very fast the main trade-off of plasmonics was built off: losses vs. confinement [5]. The more plasmons are confined to the interface, the bigger are losses conventionally associated with the process of free electron transport or displacement in metals followed by electron-electron and electron-phonon scattering. This SPPs loss channel, which exists even in the ideal case of perfectly smooth metal layer interfaces is expectedly appended by intensive scattering of surface plasmons on possible surface/bulk imperfections and defects including the ones of extremely small sizes (of a nanometer scale, like metal grains) as a direct consequence of big wavevectors of SPPs in comparison with light waves of the same frequency [6].

Thus, advancing in terms of plasmonic circuitry inevitably brings a challenge of fabrication as flat as possible interfaces. This strict constrain clashes with another requirement, often imposed on fabrication processes – to deposit ultra-thin metal layers with typical thicknesses below 20 nm. Such requirement is erected both in plasmonics and metamaterials. In the former, the losses of so-called long-range SPPs considered together with hybrid plasmonic-photonic modes as a workhorse in guiding [7] are inversely dependent on the guiding (metal) layer thickness. In the latter case, a new trend in hyperbolic metamaterials claims a metal-dielectric multilayer as the basic device possessing hyperbola-like dispersion bands [8]. In employing such device as a hyperlens, the quality of the lens, e.g. its ability to image subwavelength elements with high contrast is determined by the metal layer thickness

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and smoothness [9]. Together, both requirements impose a very challenging message for current fabrication technologies implying almost reaching the technological limits of depositing thin layers. As such, new advances in the deposition of such layers have to be made.

Conventionally plasmonic materials are associated with metals. This is because the coupling to free electrons anticipates their presence in excess in a material. From the phenomenological point of view, it means that standard solutions of Maxwell's equations for surface waves require different signs of material constants, e.g. permittivity functions, in media in contact. Accordingly to the classical model of the free electron gas – the permittivity is represented by the Drude formula, and the real part of the permittivity is negative below plasma frequency  $\omega_p$ . For typical frequencies of the visible and near infra-red (IR) ranges, such noble metals like Au, Ag, and Al are the best candidates having  $\omega_p$  further away in the ultraviolet. Sometimes, Cu is considered as well. However, despite low losses, their universality in plasmonic applications has been seriously challenged initiating a quest for alternative plasmonic materials [10, 11]. Not the last role in stimulating the search of alternative solutions plays fabrications issues: requirements for ultra-thin uniform layers as we specified above and CMOS compatibility. Silver and gold as the best so far plasmonic materials in terms of losses in the visible and near-IR possess the high surface energy leading to granulation for very small film thicknesses and challenges for low-loss adhesion layers. Also, these metals are beyond the list of materials accepted in semiconductor growth processes. Al and Cu are CMOS compatible, but in terms of losses are considered worse than gold and especially silver.

The list of alternative plasmonic materials is really vast now, see, e.g. [7] and references therein. Some of them are promising and draw a lot attention, like CMOS-compatible transition metal nitrides (TiN, TaN, etc.) [12, 13] or II–VI semiconductors oxides (InTiO, Al:ZnO, Ga:ZnO, etc.) [14, 15]. Others seem to be appropriate substitution of metals in mid- and far-IR or even in the terahertz range, where metallic properties of noble metal become too strong, and their behavior resembles more perfect conductors ousting truly plasmonic features. Here, typically heavily doped semiconductors [16, 17] and so-called two-dimensional atom-thick materials like graphene [18, 19] are considered.

Such variety of materials definitely brings a challenge in formulating common criteria for evaluation of their plasmonic performance and processing challenges. Aiming the fabrication issues in reaching ultra-thin uniform smooth layers, we put forward material

properties and fabrication peculiarities. The main parameters to be considered for improving the functionality are roughness/uniformity, range of available or demonstrated thicknesses and requirements for an adhesion or wetting layer. As for optical properties, if possible SPP loss of characterization will be given, however, in many cases, data are missing.

The structure of the review is the following. In the second section, we briefly remind deposition/growing techniques and methods for characterization film properties. The overview of advances in depositing thin metal films on various surfaces follows. Techniques for depositing gold and silver come first. Then, we describe the deposition of Al, Cu, Cr, Ni, Ti, Fe, and alkali metals pointing on their possible employment in plasmonic problems. The next section deals with transparent conductive oxides and nitrides, the main ones being ITO, AZO, and TiN. Section IV handles highly doped III–V semiconductors. Two-dimensional materials apt for plasmonic applications are considered in Section V. Prospective view on fabrication advances and conclusions are placed in the last section.

## 2 Deposition/growing and characterization techniques

In the following, we shortly overview typical fabrication techniques for depositing/growing thin plasmonic layers and approaches in characterizing the obtained structures. As the aim of the review is not a full description of the techniques, for this, a book on the subject would be more appropriate; these descriptions are to be understood as only presenting the principles of the techniques and not providing extended details of their complete capabilities.

### 2.1 Deposition/growing techniques

Generally, the deposition techniques can be divided into several categories. We will first present an overview of physical vapor deposition (PVD) techniques, then followed by a description of the chemical vapor deposition (CVD), and at the end, the techniques that are in some extent a combination of the chemical and vapor phase techniques or are based on chemical synthesis.

For metal deposition, the most used technique is *evaporation* [20, 21]. Its principle is to heat the metal to be deposited in a controlled manner. So atoms will evaporate from a target at a prescribed rate and eventually rest on the desired substrate. Depending on the equipment used,

there are two main types of evaporation techniques: electron beam (e-beam) evaporation where the metal target is heated with the help of a beam of electrons directed at the metal surface, and thermal evaporation, where metal is heated using the Joule effect. It should be noted that e-beam evaporation may be used also for depositing dielectrics.

Another deposition technique, mainly used for metals but that also could be used for dielectrics and semiconductors, is *sputtering* [20, 21]. In the process, a target material is bombarded with high-energy particles such that the atoms are knocked out from the target and reach the substrate. The most common used sputtering technique is magnetron sputtering. In this case, due to the strong electric and magnetic fields generated inside the magnetron, plasma is formed and confined close to the target material. When depositing dielectrics, there is a risk of charge accumulation, thus, generally a high-frequency variation of the anode-cathode bias is applied. In this case, sputtering is generally referred to as RF (radio frequency) sputtering.

While there exist many variations of sputtering techniques, for example, ion-beam sputtering, reactive sputtering, ion-assisted deposition, high-target utilization sputtering, and high-power impulse magnetron sputtering, unless otherwise specified, we will refer to magnetron sputtering throughout the article.

The next PVD technique is molecular beam epitaxy (MBE) [20, 21]. In this case, a target or targets are slowly heated to obtain sublimation of the desired material that will reach the substrate and be deposited there monatomically. Owing to the low deposition rate, there will be an epitaxial growth of the layers, thus, yielding a much smoother film. It should also be noted that, although it is a physical vapor deposition technique, when using more than one target, a chemical reaction on the substrate surface might take place, thus, resulting in forming of, for example, GaAs layers from separate Ga and As targets.

Pulsed laser deposition (PLD) is also a PVD technique [20, 21]. A high-power laser pulse is focused on the target material. The vaporized material then creates a plasma plume that will eventually reach the substrate and, thus, deposit material on it. Although the setup is relatively simple, due to the presence of various species (from electrons and ions to atoms and clusters) in the plasma plume, controlling the deposition characteristics is not straightforward.

Apart from the PVD techniques, there are also several CVD ones.

The most common CVD method is plasma-enhanced chemical vapor deposition (PECVD) [20, 21]. This technique is based on mediating a specific chemical reaction

in a plasma environment, thus, to deposit the desired composition on a prescribed substrate. It generally involves a high temperature and relatively complex chemistry, but it is the basic technique for graphene deposition, for example.

Another type of CVD is atomic layer deposition (ALD) technique [20, 21]. The main difference between the ALD and PECVD techniques is the chemical reaction dynamics. Thus, the ALD reaction is self-limited by the reaction dynamics and, as such, in one cycle a monolayer of a specific material is obtained.

Metal-organic vapor phase epitaxy (MOVPE) [20, 21] is a deposition technique that is based on a complex combination of vapor phase deposition and chemical reactions. As it is simultaneously chemical and physical vapor depositions, MOVPE is also called MOCVD. While in the MBE case the chemical reaction may or may not be used during the deposition, in the MOVPE, it is a necessity. The reaction between the species present in a machine creates the condition for crystals to grow, thus, enabling obtaining the desired material.

Other deposition approaches involve the use of chemical reactions in solution with a reduction of a smooth layer of material on the substrate. The *electroless* technique for depositing thin Ag layers [22, 23], and solution-dipping processes for Al [24] are examples of these techniques. They involve the reaction of at least two species in solution, and the desired material is formed and deposited on the substrate, while the by-products remain in solution.

## 2.2 Characterization techniques

The characterization techniques can be split in two main categories. On one side, the topological and composition characterization will describe the layer quality in terms of roughness, completeness, uniformity, thickness composition, etc. On the other side, the functional characterization deals with the description of the deposited layers in terms of their response to incoming radiation, electrical or chemical stimuli, etc. First, we will review the topological characterization techniques.

The main methods for determining the topology of the deposited layers are scanning electron microscopy (SEM) and atomic force microscopy (AFM). They are generally used in conjunction with each other as they produce complementary information.

The SEM is based on the interaction of a focused electron beam with a surface of interest that is scanned by the beam [25]. The emitted secondary electrons are captured by a detector, and a pixel-by-pixel image is created.

Although the obtained image is generally very similar to a topographical image of the surface, there is no direct correlation between them. As the SEM image represents the emitted electrons, it should be considered as an interpreted image. Peaks and valleys in the image are not necessary topographical ones, and the information about the axis perpendicular to the image plane is, at most, qualitative. Still, it will show, e.g. the areas where there is no coverage with the desired layer, number of particles present on the surface, etc. Sometimes, SEM techniques are combined with electron dispersion X-ray spectroscopy (EDX) technique. Using EDX, the chemical composition of the sample can be analyzed quantitatively, thus, allowing for the determination of its chemical purity and composition.

The AFM imaging uses a completely different procedure to obtain information about the structure. In this case, a sharp tip of a few nanometer curvature radius is placed in the vicinity or on top of the surface of interest [26]. While scanning the surface, the tip deflection is measured using a laser spot, and as such, quantitative information about the surface topography is obtained. However, the information obtained will not give any indication of the nature of the substrate, thus, it is hard to differentiate between areas, where the desired material is deposited and where only the substrate is present. More advanced AFM includes also the possibility of recognizing chemical species based on the interaction between the tip and the substrate.

Transmission electron microscopy (TEM) is a technique relatively similar to SEM, but in this case, the collected electrons are transmitted through the sample rather than reflected from the sample surface [27]. The main limitation of the TEM is the thickness of the sample. Thus, in order for the electrons to pass through the sample, it needs to be just several tens of nanometers thick. Various imaging postprocessing modes exist, which can provide detailed information about the sample ranging from topographical imaging to lattice parameters and chemical composition.

Scanning tunnelling microscopy (STM) is a technique where a sharp tip is scanned on top of a specimen [28]. Different from AFM, there is a bias applied between the tip and the substrate. The current that tunnels through is a function of the local density of states. As the resolution obtained is generally below 0.1 nm laterally and 10 pm vertically, STM can provide information about the atomic structure of the scanned sample.

Auger spectroscopy technique is based on exciting an atom by an external field [29]. If the external field is strong enough, a core electron may be expelled leaving a hole. Such an unstable state will lead to the decaying of an electron from the outer shell. The resulting obtained

radiation may lead to a second electron being expelled from the atom. This second electron is a so-called Auger electron, and by measuring its energy, one can determine the atomic species and, thus, the chemical composition of a specimen. Although quite complex, this technique is now routinely used for determining the elemental composition of surfaces.

X-ray photoelectron spectroscopy (XPS) is another technique for determining the chemical composition of a surface [29]. In this case, the specimen bombarded by an X-ray beam will emit electrons, and by analyzing the number of the electrons and their energy, the chemical composition of the surface can be determined.

Reflection high-energy electron diffraction (RHEED) [30] is a technique, where an electron beam is incident at a glazing angle on the surface of interest. The diffracted electrons will interfere and, as such, create patterns that will provide information about the crystal structure and lattice parameters of the specimens' surface.

From the functional point of view, there are a few techniques that are mainly used. The *four-point probe* technique is based on accurately placing four probes at predetermined distances on a substrate. Using two of the probes for providing a potential difference and measuring the current with the other two, one can accurately measure the specimen conductivity. By corroborating these measurements with the theoretically predicted ones, the electrical characteristics of the deposited layer can be estimated.

In order to characterize the behavior of surface plasmons-polaritons on thin metal films, there are several ways possible. Scanning near-field optical microscopy (SNOM) is a technique where a SPP field is measured using an AFM-like probe [31]. When the SPP is propagating along a surface, its field will decay exponentially away from the metal-air interface. By placing a probe in near vicinity of the surface, this field can be captured and measured, thus, providing information about the SPP behavior. In the same time, due to its AFM characteristics, the field distribution can be correlated to the topographical one.

Another option is to use the Kretschmann or Otto setup. As the wavevector of surface plasmons-polaritons is bigger than the one of light waves in free space, in order to excite a SPP, one has to use a high-index prism. Both Otto and Kretschmann configurations employ such prism, the main difference between the two being the type of the separating layer between the interface supporting the surface plasmon-polariton and the prism. In the Otto case, this layer is of low index dielectric, and the SPP propagates at the interface between this spacing layer and the



metal, or metal-like one. In the Kretschmann case, the metal or metal-like layer is in close contact with the prism and is actually the separating layer. The SPP propagates at the interface between this layer and free space (generally) beneath the layer. In both cases, by measuring the reflected spectra of a beam incident on the prism, one can determine the existence of the plasmon certified by dips in reflection spectra.

A third option for characterization of the layers' quality is to fabricate a waveguide and measure SPP transmission through it. By considering several waveguides of various dimensions, the propagation length of the plasmon can be deduced.

The last technique presented here is to measure the reflection and transmission spectra of a layer and, from here, determine its optical characteristics, and with more advanced measurements, the dispersion diagram of the material measured. Although reflection-transmission spectroscopy is a very powerful technique that provides important information about the layer quality, it cannot give direct evidence about the presence of an SPP at the interface. A more developed technique, but based on the same principle is *ellipsometry*. In this case, the reflection-induced ellipticity of a circularly polarized beam can provide information about optical and material properties of the film.

Although there are several other techniques, like leakage microscopy technique or electron energy loss spectroscopy, the above-mentioned ones are the most used, thus, we limited ourselves to their brief description.

### 3 Metallic films

By far, the most used materials for plasmon propagation in the visible and IR ranges are metals. Owing to their high electron mobility, they hold the promise of having the lowest losses at these frequencies. Out of the multitude of possibilities, gold, silver, and aluminum are the ones that are mainly used. Although the alkali metals are theoretically better due to their even higher electron mobility and, thus, lower losses, their notorious chemical and mechanical instability makes them impractical to work with. There have been only very few attempts where plasmons in these metals were characterized [32].

#### 3.1 Gold thin films

Gold is the plasmonic material mostly used nowadays. Its advantages are high chemical stability and electron

mobility. It can be deposited in various ways, from electron-beam evaporation to sputtering, but due to its chemical inertness, it cannot be deposited using precursors, as in atomic layer deposition machines.

Surface plasmons were theoretically predicted by Ritchie in 1957 [33], but the first experimental proof was done by Kretschmann in 1971 [34]. The method he developed is still used today as one of the methods for exciting this kind of waves. In his work, he used gold evaporated directly on the surface of a prism, thus, being able to excite the desired plasmons. Gold was used as the material of choice for exciting plasmons since then. Its biocompatibility helped in developing various techniques where surface plasmon-polaritons excited in gold films were used for enhancing Raman spectra [35] or measuring the growth of thin organic films [36]. But in the same time, the existence of surface plasmon-polaritons allowed for better characterization of the optical properties of gold [37].

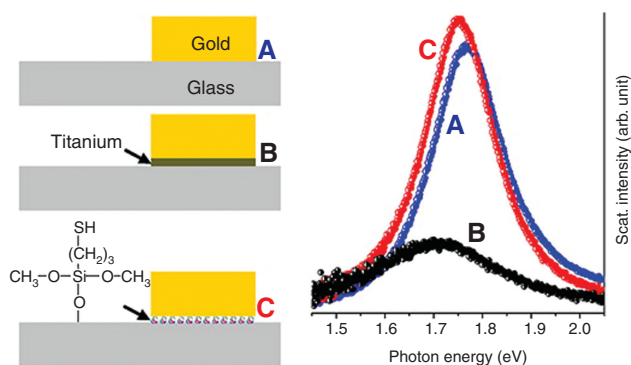
In the last 15 years, the plasmonic waveguides came to prominence due to their possibility of confining light at a scale much smaller than its wavelength. This allows, in theory, for highly compact interconnects between various optical devices. On the other hand, due to the pronounced losses in such waveguides, the characteristic propagation distance of surface plasmon-polaritons is typically very small. Thus, a compromise between the light confinement and losses must be found.

In order to avoid unnecessary losses in metal waveguides, surface roughness and the film's uniformity should be as perfect as possible. This challenged the depositing techniques to evolve in order to produce ultra-smooth metallic layers. An additional requirement on the layer thickness also targets to make them ultra-thin.

The first impediment in depositing smooth thin gold films is the high percolation threshold. The combination of high atom mobility and surface tensions effect leads to fractal-like cluster to be formed when depositing gold [38]. Owing to these effects, the thinnest complete gold layer that can be deposited on silicon or silica is in the order of 20 nm. In the same time, apart from the relatively large minimal thickness, the obtained layer is quite rough, with measured roughness up to 4 nm [39].

Various studies were made in order to understand and counterbalance this effect. The accent was put on *in situ* measurements that can allow for better characterization of the growth dynamics on Au layers. X-ray reflectivity and scanning tunnelling microscopy are the ones mainly used [40, 41] but *in situ* Auger electron spectroscopy [42] and *ex situ* pull testing [43] were also reported among others.

To reduce this high percolation threshold, the most straightforward technique is to deposit, prior to the gold



**Figure 1:** Influence of the adhesion layer on the scattering spectra of single Au nanorods. (A) bare gold layer; (B) gold layer deposited on the Ti adhesion layer; (C) gold layer on top of the mercaptopropyl functionalized surface. Reproduced with permission from [46].

layer, an adhesion layer. This way, the surface characteristics change, and gold can be deposited as thin complete layers. The downside of this technique is the introduction of an extra layer in the system, thus, potentially changing the characteristics of the structure.

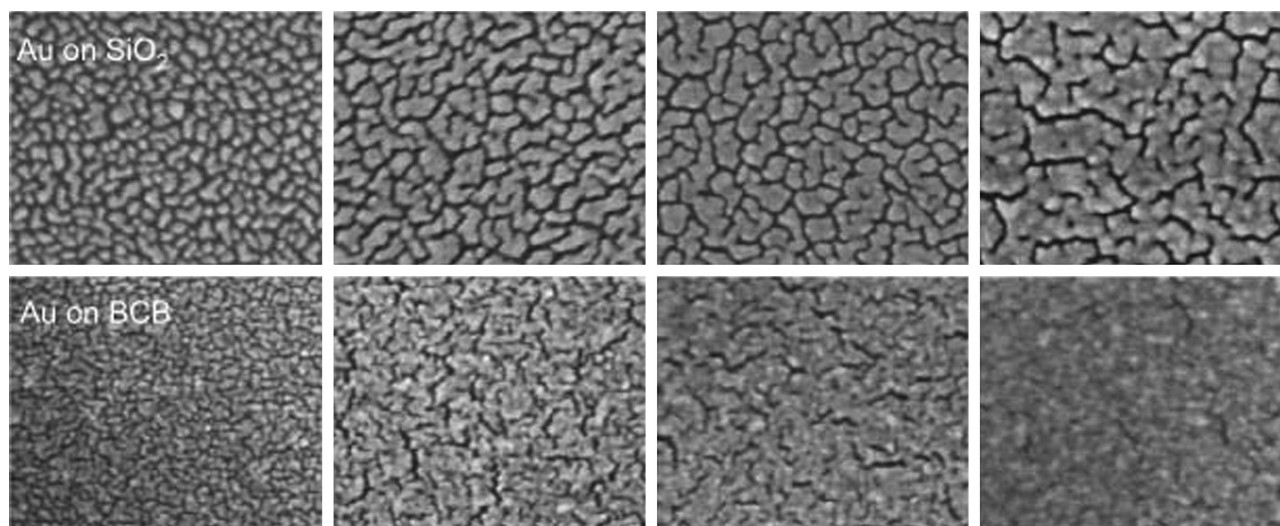
Two of the most used adhesion layers are chromium [44, 45] and titanium. Although they allow for a smoother and thinner waveguide, neither of these metals has the optical characteristics superior to gold; thus, the plasmon behavior can worsen significantly. Their use is extremely important for thin gold layer deposition, but in the same time, their influence on the plasmon characteristics increases. For example, even keeping the titanium adhesion layer to a minimum of ca. 2 nm, for a system where the gold layer is 17 nm, the contribution of the adhesion layer significantly deteriorates the overall

performance of a golden nanorod [46] (see the scattering resonances in Figure 1). Trying to reach even lower thicknesses will increase the ratio between the gold and titanium contributions, thus, the waveguide or particle characteristics will be even worse. A much less used metallic adhesion layer, which promises forming of a very smooth Au layer on sapphire is Nb [47]. In this case, the Au layer tends to be monocrystalline even at thicknesses down to 10 nm.

Polymers, on the other hand, may be used as an adhesion layer, although their influence was not thoroughly investigated. Ormocomp shows the possibility of allowing for 12-nm-thick layers to be created [48], but a systematic study was not, to the best of our knowledge, made. Another polymer layer used as a seed layer is Cyclotene (also known as BCB) [48]. Leosson et al. also show the possibility to reach thin layers with thicknesses of about 10 nm (Figure 2). Owing to the lack of comprehensive study on this topic, we cannot say anything about result reproducibility or layer characteristics.

Preliminary experiments also show that extremely thin Au films may be deposited on conductive oxides [49]. Although there are no detailed studies, layers as thin as 2.4 nm of Au may be sandwiched between two ITO layers using pulsed laser deposition methods.

Amino- and mercapto-silanes [46, 50–52] were investigated as adhesion layers. Both these organosilane compounds exhibit great promise for obtaining ultra-thin gold layers with deposition of metal performed by conventional electron beam or thermal evaporation techniques. Authors report deposition of gold on a silicon wafer pretreated with the amino-silane compound



**Figure 2:** Ultrathin (3, 4.2, 5.4 and 7.2 nm respectively) Au layers on pure silica (upper row) and on BCB polymer (lower row). Reproduced with permission from [48].

reaching a thickness of as thin as 6 nm [51] and on fused silica wafers pretreated with mercapto-silane with the mass equivalent thicknesses of 5.4 nm [52]. Optical characterization of such metal layers showed that the obtained gold layer has properties very close to the one of pure bulk gold [46, 52].

The sputtering techniques are also commonly used for depositing Au layers. Thus, using optimized sputtering, gold was deposited on silica/silicon with a surface coverage of ca. 90% and an approximate thickness of  $7.6 \pm 0.4$  nm [52]. Although the surface coverage below 100% witnesses the presence of holes in the layer, having an almost complete layer at these thicknesses on silica substrates is an achievement in itself.

In the same time, it was reported that atomically flat Au layers can be obtained on special substrates like mica [53] and LiF [54] using sputtering techniques. The obtained gold layers were very smooth, the RMS in the latter case was 0.2 nm (but the thickness was 80 nm). However, the substrates used either have too high losses for the visible or infrared ranges, as in the case of mica, or impractical (due to its toxicity) to be used in mass production as in the LiF case.

A different approach involves evaporating Au on a mica substrate and then peeling it off from the initial substrate and attaching to a silica one [55, 56]. This approach allows for extremely flat layers (RMS=0.275 nm [55]) to be created (Figure 3), but it does not preclude the use of

metallic adhesion layers in order to insure good adhesion between the silica superstrate and the gold.

Another attempt to obtain smooth layers of Au on silica involves thermal annealing of a thin gold coating in nitrogen atmosphere [57]. High temperature (up to 814°C) allows for obtaining monocrystalline Au embedded in the Si lattice. Lower annealing temperatures (350°C and 626°C) lead to nanoislands randomly dispersed on the surface without epitaxial relationship. Thus, no complete layers were formed impeding their implementation in plasmonic devices.

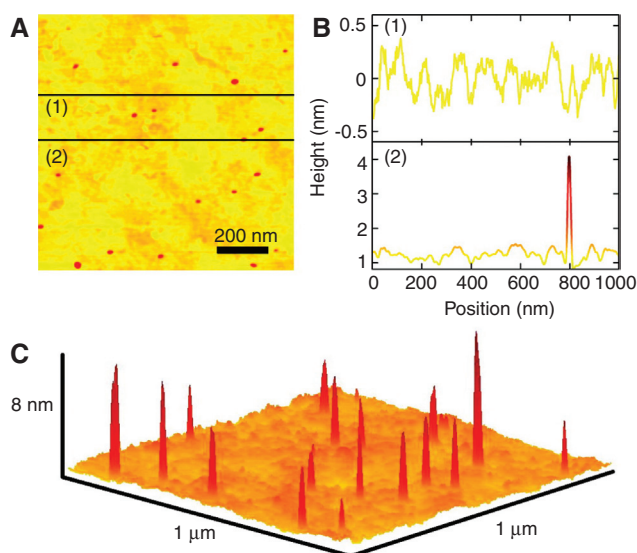
Recently, using chemical synthesis, monocrystalline gold flakes were controllably grown [58]. These flakes exhibit the ultimate smoothness but have several disadvantages. First of all, they are still relatively thick and their thickness is dependent on the size, thus, for bigger structures, they need to be thicker. Second, they are grown in solution, and when deposited on a substrate, their position is difficult to control accurately. Owing to this, the possibility for this method to be used in large-scale production is limited. A short overview of thin Au film parameters is shown in Table 1.

We should also mention that there were few attempts to deposit gold using CVD methods [59, 60]. In these cases, the gold loading is low, and no any complete layer was formed. To our knowledge, there are no CVD processes in which Au can be reliably deposited in thin films.

### 3.2 Silver thin films

Silver is another metal with huge potential in the plasmonics and metamaterials research field. Although it has theoretically lower losses than gold [10], it is less utilized due to its notorious chemical instability [61]. While gold is stable once deposited, silver, if not capped with a protection layer, oxidizes fast permanently degrading in plasmonic properties.

Most of the techniques used for improving gold deposition, optimizing the adhesion layers and the



**Figure 3:** Ultrasmooth gold layers obtained by stripping from mica substrates. (A) CdSe quantum dots on a gold layer; (B) height profiles of a flat gold layer and a layer with a quantum dot; (C) three-dimensional AFM image of quantum dots on the gold layer. Reproduced with permission from [55].

**Table 1:** Thin Au film parameters on different substrates and using various adhesion layers.

Thickness	RMS	Adhesion layer	Substrate	Ref.
10 nm	0.2–0.3 nm	Nb	C-cut sapphire	[47]
4–15 nm	1 nm		BCB,Ormocer	[48]
2.4 nm			ITO	[49]
6–10 nm	0.26 nm	Organosilane	Silicon	[51]
5.4–15 nm	0.6 nm	Mercaptosilane	Fused silica	[52]
80 nm	0.2 nm		LiF	[54]
150 nm	0.275 nm	Cr	Mica	[55]



deposition parameters as well as using different substrates, can also be employed for obtaining thin silver films. But, due to its reactivity, thin silver layers can be obtained with the bigger nomenclature of methods including electroless techniques [22, 23, 62] and CVD methods [63].

Epitaxial growth of silver films is, to our knowledge, the most advanced method to obtain thin smooth layers [64]. Thus, using a freshly cleaved GaAs (110) substrate and combination of a low deposition rate at low temperature and annealing at room temperature [65, 66] one can obtain atomically flat ultrathin silver films (Figure 4). This method also allows the determining of a critical thickness below which silver cannot be deposited as a layer: 15 Å. Although the obtained film has the ultimate flatness with a maximum height difference below 0.5 Å, it has the major disadvantage of not being a continuous layer. During the annealing process, the silver atoms rearrange and form areas of extreme smoothness but also voids where no silver is present. Still, this technique is invaluable to obtain smooth layers, and it was further developed for silicon substrates [67, 68] showing major improvements of the film plasmonic characteristics.

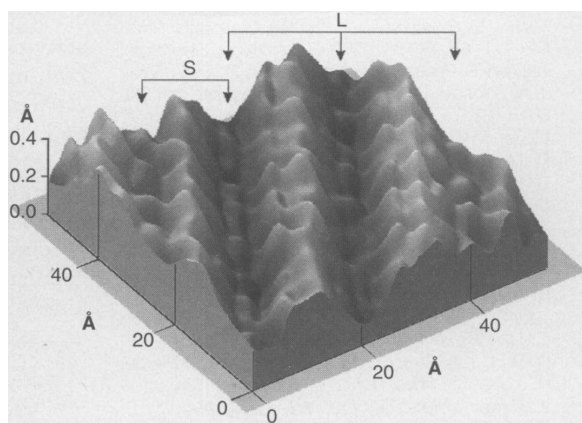
Thin silver films can be obtained also using RF magnetron sputtering [69]. In this case, the film is not monocrystalline, but rather nanocrystalline, thus having roughness in the order of 0.18 nm for a 14 nm-thick layer of silver. The roughness increases to 2.5 nm with the growth of the layer thickness as a direct consequence of the grain size enlargement. Still, it provides an extremely smooth layer that may be used for plasmonic devices. Another big advantage of this technique is the use of glass as a substrate, thus, making samples readily available for visible and IR plasmonics. Using DC magnetron sputtering [70], one can obtain monocrystalline silver layers; however,

the substrate has to be lattice matched. In the reference, mica is used as the substrate, making silver films unapt for visible/IR plasmonics.

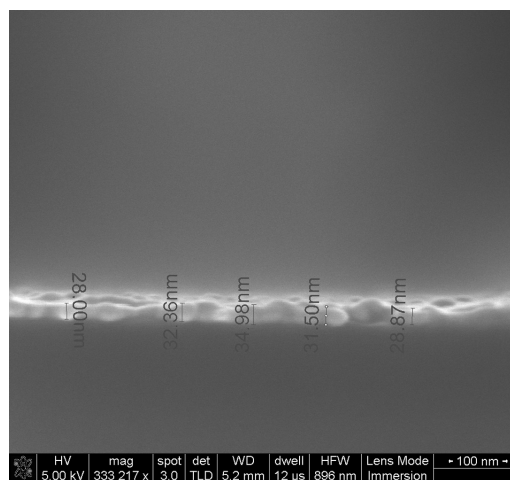
The ALD technique is also used for obtaining a thin smooth silver film [71]. This technique is extremely limited due to the narrow temperature window of a maximum 20° and the difficulty in obtaining suitable precursors. Still, it allows for conformal deposition of silver on high-aspect ratio structures. The thinnest layer obtained in this case is in the order of 10–15 nm, but it is extremely rough, an approximate roughness being above 8 nm. However, measurements of resistivity reveal that a 40-nm Ag film deposited by ALD has resistivity 6  $\mu\Omega$  cm in contrast to a 40-nm CVD-produced film with resistivity 80  $\mu\Omega$  cm.

Silver can also be deposited chemically [22, 23, 62, 72]. In this case, a reducing reaction is used to obtain thin silver films, reaching down to 10 nm thickness. The major disadvantage in this case is the small grain dimensions (Figure 5) and, thus, potentially numerous defects. Also, for very thin films, it is very difficult to obtain uniform coverage on large areas.

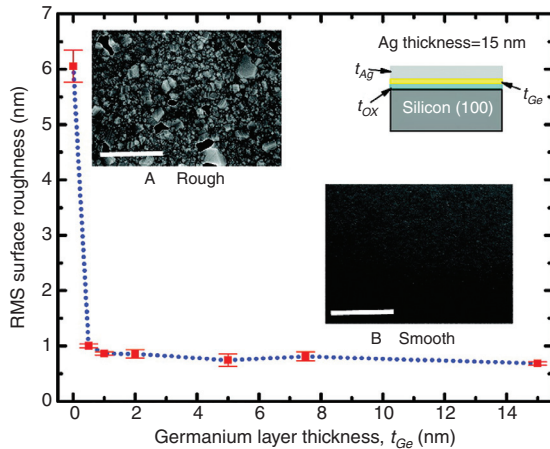
In the case where the smoothness is paramount over the optical properties, one could use Ge as an adhesion layer (Figure 6) [73, 74]. As described by Logeeswaran et al. [75], using Ge has the advantage of not only obtaining much smoother layers with up to one order of magnitude less RMS, but also increased temperature stability of such layers. Another material that can be used as an adhesion layer for silver deposition is molybdenum trioxide  $\text{MoO}_3$  [76]. As a dielectric, it brings the advantage of being utilized as an adhesion layer, reducing the losses, but still, the silver layer is not continuous. Also, up to the 0.5- $\mu\text{m}$  range, the  $\text{MoO}_3$  has relatively high losses [77]. Although



**Figure 4:** A 3D rendering of an STM image showing atomically smooth silver layers. Reproduced with permission from [65].



**Figure 5:** A 30-nm-thin Ag layer obtained using electroless techniques. Reproduced with permission from [22].



**Figure 6:** Variation of the RMS with the Ge seed layer thickness. Reproduced with permission from [73].

less used, aluminum-doped zinc oxide is a possible adhesion layer [78]. The authors claim Ag layer thicknesses down to 10 nm, and as it is a sandwich-like structure, the degradation of the layer is highly reduced. Cu is also used as an adhesion layer for depositing Ag films [79] reaching thicknesses as low as 6 nm.

As with gold [55], a promising technique for obtaining thin smooth silver layers consists of silver deposition on smooth substrates with poor adhesion (mica, silica, silicon) and covering them with strongly adhesive materials like epoxy. Peeling off the obtained layer from the initial substrate – so-called template stripping [80], produces a metal layer with roughness dictated by that of the initial substrates. The partial disadvantage of this method is the formation of only one working surface because another one can be very rough. Of course, it is not relevant if the thickness of a metal layer is exceeding 100 nm.

An interesting technique for obtaining thin silver layers with reduced roughness is the co-sputtering deposition of Ag and Al [61]. The obtained films are Al-doped Ag with doping concentrations of up to 4% that allows for smooth and thermally stable layers. The presence of Al will definitely influence the optical characteristics [61], but its influence will probably be minimal compared to the one of, e.g. Ge wetting layer due to the better optical properties of Al with respect to Ge.

Last, smooth silver films can be pressure induced [6]. In this case, the RMS is 1 nm or even below down to an impressive 0.1 nm, but the resulting thickness of the Ag layer is not well defined. Also, the area with smooth silver is determined *a posteriori*, and it cannot cover the whole wafer, but only specific parts. Last, no any optical characterization of such films' appropriateness for plasmonic applications has been performed so far. An overview of Ag thin films may be found in Table 2.

### 3.3 Aluminum thin films

Aluminum as a plasmonic material has some advantages, for example, the deep UV position of the plasma frequency, high carrier concentration, and CMOS compatibility. In terms of losses, it is worse than silver and gold, but still falls in the range of reasonable materials in plasmonic applications. There are comparatively very few articles where aluminum is applied as a plasmonic metal, and as such, techniques for depositing extremely thin films have not been fully developed. Thus, an ISI Web of Knowledge search for articles that include aluminum together with the keywords plasmon or metamaterial gives a total

**Table 2:** Thin Ag film parameters on different substrates and using various adhesion layers.

Thickness	RMS	Adhesion layer	Substrate	Ref.
100 nm	1 nm	By pressure	Si	[6]
6 nm	0.37	Al doped	Silica/Si	[61]
45 nm epitaxial	0.36 nm		Silicon	[64]
50 nm thermal	3.27 nm		Silicon	[64]
1.5 nm	Atomically smooth		GaAs	[65]
80 nm monocrystalline	0.37 nm		Si	[68]
80 nm polycrystalline	2 nm		Si	[68]
14–300 nanocrystalline	0.18–2.5 nm		Glass	[69]
97 nm monocrystalline	0.82		Mica	[70]
10–20 nm	0.4 nm	Ge	Silica	[73]
5–8.5 nm	0.22–0.73 nm	Ge	Silica	[74]
15 nm	0.6 nm	Ge	Silica/Si	[75]
10 nm		AZO		[78]
6 nm	0.4 nm	Cu	Silicon	[79]
30–280 nm	0.65 nm		Mica, Si, silica	[80]

slightly above 1335 articles in the last 15 years. Meanwhile, the same search, but with silver, gives one order of magnitude larger number of articles, namely almost 15,000 articles, and gold plasmon or metamaterial search almost doubles the latter number, reaching about 26,000 articles.

Owing to its CMOS applicability, the research in depositing thin aluminum films is not confined only to plasmonics and metamaterials. Thus, we present in the following the various methods that could be used for depositing thin Al films.

Initial studies show that evaporated aluminum might form a continuous layer even at thicknesses as low as 4 nm [81]. Generally, for plasmonic experiments, an aluminium film deposited by an e-beam or thermal evaporation is above 20 nm in thickness [82]. One certain plasmonic application of an ultrathin Al layer for guiding hybrid long-ranged SPPs was reported in [83]. The thickness of the layer deposited by evaporation was 15 nm. Unfortunately, no any material characterization data of the metal layer structure were provided.

A low-cost chemical way to deposit aluminum is reported in [24]. It is called the solution-dipping process and is based, in fact, on a two-step procedure with first catalytic treatment of the substrate and then immersing it in an aluminum precursor solution. The obtained films have a minimum thickness of ca. 15 nm and relatively low roughness. As the authors are intending to use these films for electrical interconnects, the films were characterized in terms of the electrical sheet resistance. More studies to show the possibility of using this simple and effective process in plasmonic-related applications are needed.

Dubois et al. [84] reported on the possibility of CVD deposition of Al from precursors through thermal decomposition. The deposition rate was ca. 100 nm/min, thus, theoretically allowing the possibility of reaching layer thickness below 10 nm. However, there are, to the best of our knowledge, no reports of attempts to minimize the aluminum film thickness.

Aluminum can be also deposited by laser-assisted CVD as in [85]. In this case, the deposition rate of aluminum is comparable to the one of conventional thermal CVD, but further studies are needed to ascertain the possibility of using these films for photonics and especially plasmonics.

Another technique used for depositing thin aluminum films is sputtering. Metals sputter easily; thus, it is not surprising that magnetron sputtering of aluminum is a well-known technique [86–88]. This technique allows for layers of tens of nanometer thickness at least but, up to this date, has not been used in plasmonic research.

Monocrystalline aluminum was successfully deposited on GaAs substrates using the MBE technique [89]. The authors mention thicknesses ranging from 30 to 100 nm.

The main advantage of this technique is the monocrystalline growth; thus, theoretically, lower losses for plasmon propagation can be presumed. One big disadvantage of this deposition is the substrate: GaAs, although having high transmittivity in the IR region, cannot be used in the visible part of the spectrum. To our knowledge, no plasmonic experiments with these films have been performed.

### 3.4 Other metals

Apart from the three metals mentioned, there have been very few attempts to use other metals for plasmonic purposes. This is mainly due to the high losses other metals have or, in the case of alkali metals that might provide lower losses, their instability. Only copper deposition has been more or less addressed due to its CMOS compatibility. Nevertheless, even simple analysis of SPP losses on a metal-dielectric interface showed that copper as a plasmonic materials leads to less losses in the near-infrared range than Al [90]. In addition, technologically, Cu is replacing aluminum as the material for interconnects. So far, initial experiments with copper-based structures have been reported [91, 92], but definitely, deposition of thin copper layers is still at the beginning.

Other metals have been addressed rather sporadically. There are some publication about iron [93], nickel [94], and chromium [95] deposition, but no thorough investigation of thin layer deposition of such metals for plasmonics has been performed. This is also due to the theoretically predicted very high losses these metals would have, thus, making them impractical for commercial devices. A very short overview of alternative metals is given in Table 3.

## 4 Transparent conductive oxides and conductive nitride films

Another class of materials that is more and more popular for plasmonic structures is the transparent conductive oxides (TCOs). Although the TCOs have not such a big negative

**Table 3:** Other metallic thin film parameters on different substrates and using various adhesion layers.

Material	Thickness	RMS	Adhesion layer	Substrate	Ref.
Al	15 nm			Soda lime glass	[24]
Al	4 nm			Glass plates	[81]
Al	30–100 nm	3.6 nm		GaAs	[89]
Cu	15 nm			TiO <sub>2</sub>	[92]

permittivity as noble metals, their losses are comparable, especially in the IR range, making them a competitive alternative to noble metals. One more advantage is the possibility of tuning their permittivity by design through deciding the dopants or the ratio of different components [13, 96], thus constituting an advantage over metals having the fixed permittivity values. By exploring this tuning possibility, plasmonic modulators where the TCOs are the active parts were investigated theoretically [97] and experimentally [98].

#### 4.1 Indium tin oxide films

Indium tin oxide (ITO) is the most used TCO nowadays. One of the main advantages of ITO is that its plasma frequency can be tuned through varying the proportions between  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$  [12, 96] or by the deposition and annealing conditions (see [10] and references therein). Although the ITO plasma frequency is in the near-IR range [12, 17, 99, 100], due to low losses, ITO could be used for plasmonic metamaterials in certain frequency ranges above the plasma frequency [10] and as an active material in plasmonic modulators [101–104] or as infrared antennae [105].

The main technique for depositing ITO is magnetron sputtering, and the properties of the obtained thick films are thoroughly investigated [106–115]. Using this technique, films with thicknesses as low as 10 nm may be deposited [98, 116], although their uniformity was not investigated.

Other methods for depositing ITO include PLD [49] with a reported thickness of 30 nm (Figure 7) and thermal evaporation [117, 118] techniques. In the latter case, the ITO thickness was between 50 and 110 nm.

#### 4.2 Other conductive oxide films

Apart from ITO, there are several other TCOs that have been tested as possible plasmonic materials for the IR range. Zinc

oxide-based TCOs are among the ones mainly used. Initial experiments with aluminum doped [78], gallium doped [119], indium doped [120], tin doped [121], or pure [122] zinc oxide have been performed. Apart from the zinc oxide-based TCOs, niobium-doped anatase titanium oxide [123] or indium-doped cadmium oxide [124] were investigated. Still, their properties in the IR range are not fully understood in order to be a weighty alternative to metallic layers.

The deposition technique mainly used for obtaining thin layers are similar to the ones for ITO; thus, magnetron sputtering is the main one [125–127]. Other methods for depositing TCOs, include PLD [123, 128–131], ion beam sputtering [122, 132], and pulsed filtered cathodic arc deposition [124].

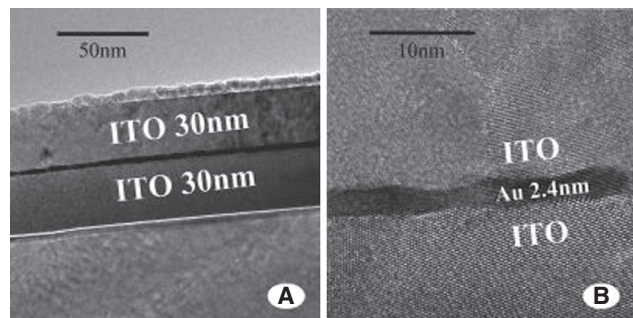
#### 4.3 Interstitial metal nitrides

Recently, films made of nitrides (titanium nitride, zirconium nitride, tantalum nitride, and hafnium nitride) have gained more prominence in the plasmonics research [133]. Their typical working wavelength range, in order to be used for plasmonic effects, is in the IR. The main appealing properties of nitrides are CMOS compatibility, mechanical hardness, and high-temperature resistance, neutrality toward biological objects and the possibility of fine tuning of parameters by adjusting conditions of deposition. There are plenty of technological approaches to deposit nitrides films. For example, by magnetron sputtering, TiN layers of thicknesses between 30 and 50 nm can be obtained. Excitation of surface plasmons on such interfaces were reported [134].

### 5 Other types of thin films for plasmonics

#### 5.1 Highly doped semiconductor films

Recently, the possibility for growing highly doped semiconductors allowed the plasma frequency of these layers to be in the range of 100 THz [135, 136]. So far, it has not yet reached the near-IR nor visible range due to the effects of doping compensation appearing at very high doping levels. However, the latest quest for mid-IR plasmonics and photonics makes the highly doped semiconductor as one of the promising candidates to substitute noble metals. Large bandwidth tunability of the plasma frequency in semiconductors by the doping level, for example, between 6 and 16  $\mu\text{m}$  [137], also raises expectations for



**Figure 7:** Low roughness 30-nm-thick ITO layers. Reproduced with permission from [49].



semiconductor plasmonics. Nowadays, there are significant efforts toward reaching higher doping levels [138–140] thus, pushing plasma frequencies up in the range of hundreds of THz and further.

The main advantage of these films is the growth methods. Thus, highly doped semiconductors are generally grown using epitaxial methods like molecular beam epitaxy [135, 137], metal-organic chemical vapor deposition [141], or metal-organic vapor phase epitaxy [142, 143]. These techniques allow for atomically smooth layers, greatly reducing the influence of roughness in the devices. On the other hand, epitaxial growth is possible only on lattice-matched substrates. As such, the substrate is generally the same base material but with lower doping levels. In Table 4, we summarize both highly doped semiconductors as well as TCO parameters used for plasmonics.

## 5.2 Graphene and other 2D materials

The ultimate thickness of a material is one monoatomic layer. With monoatomic arrangement of atoms, no any three-dimensional lattice can be constructed. Therefore, until recently, it was thought not to be possible to obtain such materials, but, with the discovery of graphene, a one monolayer of carbon, this limit was achieved. It proclaimed that the era of two-dimensional materials, whose lattices or atom packaging are confined in-plane, had begun. Among a bunch of several exceptional mechanical and electronic properties of graphene, the one which attracted a lot of attention toward graphene plasmonic applications is the possibility of actively doping the monolayer. Thus, light-matter interactions can be accurately

controlled through the gating voltage giving the possibility to obtain tunable devices [145–147].

Although there are several ways of obtaining graphene [148], the most used two are through exfoliation from graphite [149, 150] and using CVD techniques on Cu [151] or Ni [152] substrates.

The main advantage of the graphite exfoliation technique is the possibility of obtaining large areas of high-quality monocrystalline graphene on, in principle, whichever substrate. However, the obtained flakes are difficult to position precisely in case of needed alignment, and the flakes sizes are quite random.

On the other hand, CVD techniques have the possibility of wafer-scale manufacturing. The disadvantage lies in the difficulties for obtaining big monocrystalline domains; thus, the graphene response will be highly influenced by the borders of these domains. Techniques for improving the contacts between two domains with different crystallographic orientation joints are currently investigated and might lead to the use of graphene as plasmonic material. Another disadvantage due to the growth method is a substrate. When using CVD techniques, the substrate generally needs to be metallic; thus, further steps have to be made in order to transfer the obtained layer on the desired substrate. These steps will also lead to the introduction of defects in the layer, both physical, through cracks and folds, and chemical, through unwanted doping. Recently, a CVD technique for graphene on silica was developed [153], thus, expanding the substrate range.

Besides graphene, a family of two-dimensional materials with monoatomic arrangement of atoms has potentially emerged. For example, boron nitride, molybdenum bisulfide, and tungsten sulfide [148] are possible candidates to achieve controllable, wafer-scale monoatomic thicknesses. Nevertheless, these types of two-dimensional materials have only recently appeared in the focus of investigation, and their comprehensive optical characterization is yet to be done. It is interesting that two-dimensional materials put fabrication challenges to the reverse extreme, when having a monolayer processing more or less established the problem is how to fabricate a few layers thick uniform materials with prescribed sizes.

**Table 4:** Alternative material film parameters on different substrates and using various adhesion layers.

Material	Thickness	RMS	Adhesion layer	Substrate	Ref.
ITO	30	0.612 nm	Au	Glass	[49]
ITO	30	0.437 nm		ITO	[49]
AZO	21.9 nm			Glass	[78]
ITO	10			Si <sub>3</sub> N <sub>4</sub>	[98]
ITO	10			Quartz	[116]
ZnO	20–45		Ag	Glass	[122]
ZnO	35			ZnO	[122]
GZO	25–147 nm			Al <sub>2</sub> O <sub>3</sub>	[130]
ZnO	15–50 nm		Cu	Glass	[132]
ZnO	15–50 nm			ZnO	[132]
TiN	30–50 nm			GaAs	[134]
GaAsSb		0.2395 nm		InP	[141]
InGaAs	80 nm			AlInAs	[144]
AlInAs	80 nm			InGaAs	[144]

## 6 Conclusions

The definition of ultra-smooth or ultra-thin layers is subjected to functionality of a concrete device or an operational frequency range. Thus, what can be ultra-smooth in one case can be extremely rough in another. Here,

we have reviewed the techniques for fabricating layers that can be considered extremely smooth for visible and infra-red radiation thus aiming at the average roughness below 1 nm and layers thicknesses ideally below 10 nm. Such layers would allow for lower losses in devices that are based on plasmon propagation and localization or metal-dielectric metamaterial performance, thus, helping in pushing plasmonic-based devices toward the market.

Obtaining films with the prescribed thickness and smoothness that nowadays devices require is not, by any means, an easy task. For each specific material, there are several approaches that may lead to extremely smooth, ultra-thin layers; however, there is no ideal universal solution to date. In the above, we have tried to summarize the main types of plasmonic materials and the deposition techniques that allow for ultra-smooth and thin layers to be obtained.

As a word of caution, the losses in plasmonic devices can be minimized only to their theoretical limit. There are already critical works that speculate that even the theoretical limit might not be low enough for market applications [154, 155]. We believe that, although the losses might not reach the desired level for many applications, improving the techniques for depositing ultra-thin layers is a worthwhile task in maturing nanotechnology in itself. A smoother and thinner layer may lead to better performances, thus, allowing for some plasmonic devices and circuit components with specific functionalities to be developed at the level of commercial implementation.

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